Mercaptopropyl Al–Mg phyllosilicate: Synthesis and Characterization by XRD, IR, and NMR

Maguy Jaber, Jocelyne Miehe-Brendle, and Ronan Le Dred
Laboratoire de Matériaux Minéraux, UMR-CNRS 7016,
Ecole Nationale Supérieure de Chimie de Mulhouse, Université de Haute Alsace,
3, rue Alfred Werner, 68093 Mulhouse Cedex, France

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Adsorbent material with a layered structure was obtained at room temperature. The synthesis involves the reaction of three ethanolic solutions (3-mercaptopropyltrimethoxysilane, aluminum acetylacetonate and magnesium nitrate). This is the first example of organophyllosilicate having Al in the tetrahedral and octahedral sheets. The presence of thiol functions in the framework was confirmed by FT-IR.

Elaboration of adsorbent materials that can remove heavy metal ions from soils and water is an essential objective for environmental applications. Many works were developed based on covalent grafting of chelating agent on the surface of many smectites (montmorillonite, beidellite) and silica gels.[1] The grafting of organic units onto walls of the mesoporous molecular sieve has been also reported.[2] Recently lamellar hybrid inorganic-organic materials containing complexing agent in their interlayer space were described.[3–7] They were obtained by the sol–gel process at room temperature. The organic functionalities were covalently bonded to the silicate sheets. The interlayer space depends not only on the type but also on the length of the organic molecule (R) incorporated in the phyllosilicate. Till now, this route was only developed for the synthesis of organotalc and organopyrophyllite. No exchange properties are present in these materials and no acidic sites too.

This work focuses on the synthesis of organophyllosilicates containing at the same time silicon, aluminum and magnesium. The presence of aluminum in both sheets has several effects. First it leads to the presence of interlayer cations which balance the negative charges created by the isomorphic substitution of both silicon and magnesium. Secondly, it allows the tailoring of the hydrophobic–hydrophilic balance through the rate of substitution in the tetrahedral sheet. This opens new fields of applications, especially in the field of ion exchanges.

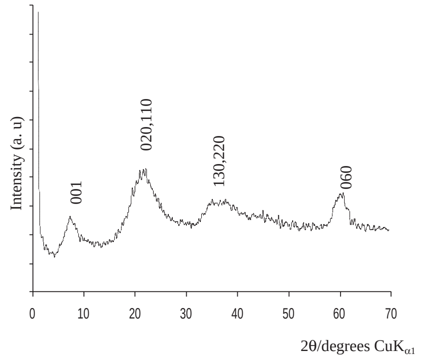

Figure 1. XRD pattern of the as-synthesized material.

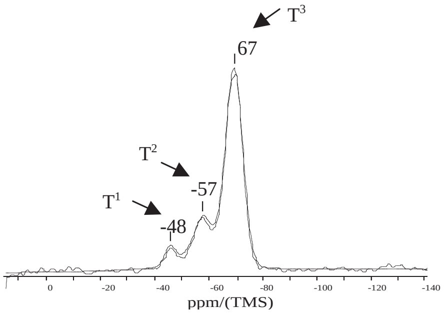

Figure 2. ^{29}Si MAS NMR spectrum of the as-synthesized material.

Mercaptopropyl Al–Mg organo-phyllosilicate was synthesized starting from a gel having the following molar composition: $RSiO_{3/2}$: 0.05Al_2O_3: 0.83MgO: 81.5$(CH_3CH_2)_2O$: 0.875Na_2O.

To prepare the solid, three ethanolic (CH_3CH_2OH Prolabo, wt%, 99.8) solutions of aluminum acetylacetonate ($[CH_3COCH\text{-}COCH_3]_3Al$ Aldrich, wt% 99), magnesium nitrate ($Mg(NO_3)_2 \cdot 6H_2O$ Carlo Erba, wt% 98) and 3-mercaptopropyltrimethoxysilane ($SH(CH_2)_3Si(OCH_3)_3$ Aldrich, wt% 96) were mixed and stirred till the formation of a clear solution. The precipitation was ended by a fast addition of 70 ml of sodium hydroxide (NaOH Fluka, wt% 97). The precipitate was kept under stirring for 24 h at room temperature. The solid was recovered by filtration, washed with water and then dried at 60 °C for 24 h.

X-Ray diffraction shows a well-crystallized organophyllosilicate. The $d_{(001)}$ value equals 12 Å. Assuming that the silicate layer thickness is equal to 9.6 Å and that the length of the organic group R is 5.43 Å, the $d_{(001)}$ value should be equal to 2R + 9.6 Å if the organic chains are perpendicular to the sheets. The obtained value suggests that the organic chains are bonded to adjacent lamella and the chains are either alternatively distributed or

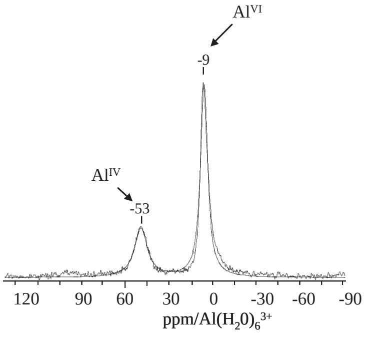

Figure 3. ^{27}Al MAS NMR spectrum of the as-synthesized material.

identically inclined in the interlayer.

The infrared spectrum of the original matrix showed a sequence of bands in agreement with the presence of organic moieties bonded to the inorganic network with absorptions at 2900 and 1180 cm^{-1} associated with ν (C–H) and ν (Si–C), respectively. A very weak signal was observed at 2560 cm^{-1} and is attributed to the SH groups related to the carbon chain.

^{29}Si NMR of the as-synthesized material provides information about the nature of the attachements of pendant groups on silicate hybrids and thus the degree of condensation between silicate sheets. Three signals at -67, -57 and -48 ppm are associated with R-Si-$(OSi)_3$ (T^3), R-Si-$(OSi)_2$-OH (T^2) and R-Si-(OSi)-$(OH)_2$ (T^1) groups, respectively, which were quantified by deconvolution of the peaks to give 75.59, 14.27 and 10.14%. This suggests a high degree of condensation.

^{27}Al MAS NMR spectrum exhibits the repartition of the aluminum in both tetrahedral and octahedral sheets. The signals at -9 ppm and -53 ppm correspond respectively to the hexacoordinated and tetracoordinated aluminum.

Further structural informations and studies on the retention of heavy metals in the interlayer by means of thiol functions are under progress.

References

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